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COMPLETE SPECIFICATION

A Process for the Preparation of Fertilizers

We, SUMITOMO CHEMICAL CO., LTD., a corporation of Japan, of 15, 5-chome, Kitahama, Higashi-ku, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for producing a NK fertilizer (i.e. containing nitrogen and potassium but not phosphorous). More particularly the present invention relates to a process for producing a urea-calcium sulphate-containing, granular NK fertilizer which has good granulation properties and possesses a very low degree of caking and hygroscopicity.

The demand for granular NK fertilizer for use as a top-dressing fertilizer or a vegetable fertilizer has recently increased. Ammonium sulphate, ammonium chloride, ammonium nitrate and urea are known nitrogen sources for such fertilizers and known potassium sources are potassium chloride and potassium sulphate. Urea has so high a nitrogen content and potassium chloride is so cheap that they are commonly used. However, both urea and potassium chloride are very hygroscopic and when both of them are used together the hygroscopicity is even greater.

Conventional granulating processes for producing granular NK fertilizers are, for example, the wet-kneading granulating and neutralising granulating processes. The wet-kneading process is a process in which ammonium sulphate and potassium chloride (or potassium sulphate) are generally used as the main raw materials. Urea and ammonium sulphate are added to them to improve granulation, a part or all of the raw materials are added, in the form of a slurry, and mixed into a large amount of recycled powdery granules and the mixture is granulated while being tumbled in the presence of a suitable amount of water. The neutralising granulating process is a process in which ammonium sulphate and potassium chloride (or potassium sulphate) are also generally used as the main raw materials and slurry-like substances obtained by reaction of ammonia with sulphuric acid, a recycled powdery granules, sulphuric acid and gaseous ammonia are fed together with said main raw materials to a granulating system and the mixture to be granulated is tumbled while carrying out an ammoniating reaction.

The granulated product produced by such processes is usually treated in a rotary cylindrical drying apparatus and/or a cooling apparatus and is then screened from under and oversize material to produce the required granular product and the undersize and crushed oversize material is recycled to the granulating system.

However, when the wet-kneading granulating process is used, the granulating temperature is so low and the water content so high that the amount of recycled material is large and therefore the apparatus for drying the granulated product and other necessary equipment have to be on a large scale.

On the other hand, when the neutralising granulating process is used, the granulating treatment is carried out at a comparatively high temperature and a part of the water introduced into the granulating system is evaporated by the heat generated by the neutralisation reaction. In this way, a granular product of a comparatively favourable properties is obtained. However, the efficiency of absorption of ammonia in the granulating system is so low that equipment for the recovery of the unreacted ammonia gas becomes necessary. Moreover, the reaction of sulphuric acid with ammonia

[*Price 5s. 0d.*]

is so rapid that local overheating is likely to occur. Therefore, the granules produced are likely to deteriorate. In addition, the jet nozzle for blowing ammonia into the granulating system clogs and the fertilizer salt adheres to the inside walls of the apparatus with the result that the operating efficiency is not very high.

Another disadvantage which arises with these processes is that ammonium sulphate, potassium chloride and potassium sulphate are difficult to granulate and the yield of product having the desired particles size is very low. Other disadvantages are that the product is very hygroscopic and will, therefore, be liable to cake during storage and that many soluble sulphates are also contained in the product which will acidify the soil and therefore reduce the value of the product.

Finally the granules produced immediately after the granulating treatment, are so soft and, in particular, the semi-granular product is so soft at temperatures near the granulating temperature that they are likely to be crushed and damaged during the cooling step.

In order to overcome these disadvantages we have carried out studies to find a process for producing an NK fertilizer which has good granulation properties and a low degree of caking and hygroscopicity. As a result, we have found that such a fertilizer can be granulated by performing a tumbling treatment on a liquid mixture of potassium chloride, urea and water in the presence of calcium sulphate. We have found that, when a liquid mixture of urea, potassium chloride and water, with or without gypsum, is formed and the liquid mixture is sprayed and mixed as uniformly as possible into either recycled material obtained from a previous preparation after the granules of desired size are separated, or into a mixture of said recycled material and potassium chloride or gypsum or urea or any mixture thereof, and the mixture granulated by tumbling in a rotary cylinder, granular fertilizer possessing good granulation properties and low caking properties is obtained. We have also found that, when the recycled material is divided into two parts and the first part used as above described, the second part mixed with the granulated product obtained using the first part and the resulting mixed granulated product cooled in a rotary cylindrical cooling apparatus, the final granulated product is efficiently cooled.

In accordance with the present invention there is provided a process for the preparation of a granular NK fertilizer which process comprises spraying a liquid mixture of 20—90% by weight of urea, 2—50% by weight of potassium chloride, 0—40% by weight of gypsum (calculated as the anhydrous salt), and 1—10% by weight of water onto solid material in a rotary granulating cylinder, the solid material being (a) a recycled material, obtained from a previous preparation of such granular material after granules of desired size have been separated therefrom or (b) a mixture of said recycled material together with one or more of potassium chloride, gypsum and urea the nature and proportions of all the components being such as to produce a product containing 20—90% by weight of urea, 2—50% by weight of potassium chloride and 5—40% by weight of gypsum (calculated as the anhydrous salt).

The liquid mixture which is to be introduced into the granulating system is usually prepared by heating the urea, potassium chloride, water and optionally gypsum. The urea may be used in a form of powder, crystals, granules or as molten material having a water content of less than 10% by weight.

When a mixed system of urea, potassium chloride and water is heated and melted, the eutectic temperature is lower than that encountered in a urea-potassium chloride bicomponent system. Thus, when a mixture of urea and potassium chloride of which the latter constitutes 12% by weight is heated and melted after the addition of 3% by weight of water, the eutectic point is 10°C. lower than that of the same mixture of urea and potassium chloride in the absence of water.

The melting point of gypsum is higher than that of urea or of potassium chloride, but when the gypsum is mixed into a mixture of urea and potassium chloride or a mixture of urea, potassium chloride and water and the resulting mixtures are heated and melted, the gypsum easily melts at the eutectic temperature of the urea-potassium chloride bicomponent system or the urea-potassium chloride-water tricomponent system.

In the process of the present invention, the liquid mixture is preferably prepared by melting a mixture of the ingredients by heating to 90° to 130°C.

If the potassium chloride content of the liquid mixture is less than 2% by weight, the eutectic point is too high whilst if potassium chloride content is greater than 50% by weight the solids content in the melted mixture increase and trouble is likely to occur when the melted mixture is pumped and when it is sprayed into the granulating system.

If the water content of the liquid mixture is less than 1% by weight, the eutectic temperature rises to such an extent that the amount of biuret formed by decomposition of the urea increases, whilst if the water content is more than 10% by weight, the amount of water fed to the granulating

system is so large that it is necessary to dry the granulated product. Whilst the water content of the mixture may partly evaporates during melting it is preferred to keep the water content of the mixture within the range of 0.7 to 10% by weight. In the melted mixture of the urea-potassium chloride-water system, the water may be supplied by adding it as much but if in addition the melted mixture also contains gypsum, the water can be supplied in the form of the water of crystallisation which is liberated from gypsum on formation of a double compound of urea and gypsum in the melted mixture. Water in these systems can also be supplied by the water present as contaminate impurity in the raw materials. However, the water is supplied (in suitable form) to keep the water content of the melted mixture within the range of from 1—10% by weight.

The reaction of gypsum with urea produces urea-calcium sulphate in the liquid mixture and/or in the granulated product. When the gypsum content of the liquid mixture is more than 40% by weight, the viscosity of the liquid mixture increases to such an extent that pumping there of to the granulation system becomes difficult. The formation of urea-calcium sulphate will vary depending upon the method of addition of the raw materials, upon the rates of mixing of those materials and upon the time of contact. In general 60—90% by weight of the gypsum forms the double compound. A mole ratio of urea to gypsum of from 4:1 to 7:1 in the product is preferable.

The liquid mixture is sprayed, preferably under pressure so as to mix it into the recycled material (optionally together with urea, potassium chloride and/or gypsum) as uniformly as possible. The pressure employed in the spraying step may range from 0.1 to 5 kg./cm^2 gauge. When the liquid mixture is uniformly mixed with the recycled material, the greater part of the urea and/or urea-calcium sulphate and potassium chloride will crystallise and, in so doing, liberate heat. Thus the granulation treatment is carried out under conditions of controlled water content and at a comparatively high temperature.

All of the potassium chloride may be incorporated in the liquid mixture or, alternatively, a part of it may be added to the granulating system as a solid raw material. The gypsum can be added to the other components before forming the liquid mixture added and mixed directly into the granulating system or added both to the liquid mixture system and to the granulation system. In each case, it is necessary to add gypsum in such an amount that gypsum content of the granulated product is kept within the range of 5—40% by weight calculated as the anhydrous salt. If the concentration of gypsum is less than 5% by weight, the granulation properties will be poor, the content of urea-calcium sulphate in the product will be too low and the degree of cracking and hydroscopicity of the product will be too high. On the other hand, if the concentration of gypsum is greater than 40% by weight, not only will the amount of free gypsum increase but also the content of effective components in the product will be reduced.

The amount of the recycled product which is to be fed into the granulating system may be 50—90% by weight, based on the total weight of all of the components added to the granulating system.

The relationship between the water content and temperature in the granulating system will vary depending upon the urea, potassium chloride and gypsum content. For example, for a composition in the granulating system which is 51% by weight of urea-calcium sulphate, 36% by weight of potassium chloride, 8% by weight of urea, 3% by weight of gypsum (calculated as anhydrous salt) and 2% by weight of water, the granulating temperature is 82°C. The higher the granulating temperature the lower will be the water content in the granulation system, but also the form of the produced granule will suffer. Therefore, it is desirable that the water content in the granulation step should be from 1—2% by weight. The granulating temperature may range from 50—100°C. and the time required for the granulation may range from 3—20 minutes.

During the granulation step the heat generated is not sufficient to cause local overheating and the granulation system is uniformly heated. Therefore the granulation step can be easily carried out on systems having a low water content at a comparatively high temperature to produce spherical granules having a smooth surface. Moreover, the use of drying apparatus is unnecessary.

The granulated product may be effectively cooled in a rotary cylindrical apparatus and a portion of the recycled product added and mixed into the granules produced as the product is cooled. In this way, mechanical crushing and powdering of the granules of the product during the cooling step is minimised. If the granules produced are mixed as uniformly as possible with the recycled material, the granules are protected by the recycled material and cushioned even if the product is mechanically unstable immediately after the granulation. Moreover, the granules are shaped by the action of coating with the recycled product. If the granulated product, which is fed into the cooling apparatus at a comparatively high temperature, is cooled slowly by admixture

with the recycled product, and by the cooling action of a cooling gas, cooling is carried out more uniformly.

In this way, it has also been found that the adhesion of the fertilizer to the inside walls of the cooling apparatus can be markedly reduced.

The amount of the recycled product which is admixed with the granulated product is preferably 10—40% by weight, based upon the total weight of product removed from the granulation system. If the amount of the recycled product is greater than 40% by weight, not only will the shape of the granules of the product be less desirable but also the size of the recycling system equipment will have to be increased. If the amount of recycled product is less than 10% by weight, the cushioning effect of the recycled product is insufficient to protect the granular product.

The cooled granules are then sieved so as to separate granules having the required size. In the seiving step, granules of desired size are separated by sieving and residue is recycled to the granulating system as it is or after partly crushing.

The end product obtained by the process of the present invention is an NK fertilizer in which the diameter of the granules may be such that the will pass a 6 to 12 mesh screen (Tyler Standard). The fertilizer will have a composition of 20 to 90% by weight of urea, to 50% by weight of potassium chloride and 5 to 40% by weight of gypsum calculated as anhydrous salt. This gypsum is mainly present in the form of urea-calcium sulphate.

The present invention will now be further described with reference to the following Examples. In the Examples, the parts and percentages are by weight unless otherwise specified.

The degree of caking in the Examples was determined as a measure of the strength of caking by erecting a hook made of stainless steel in the centre of a beaker-shaped vessel made of wood, charging the space around the hook with a fixed amount of a product sample, then applying a fixed pressure to the sample under a constant temperature and humidity, pulling out the hook embedded in the sample after the lapse of a fixed time and measuring the force (weight in kg. of the weight) required for the pull.

EXAMPLE 1

500 parts of urea (46.0% of nitrogen), 300 parts of potassium chloride 61.0% K_2O) and 250 parts of gypsum ($CaSO_4 . 2H_2O$) were mixed and heated to obtain a fluid uniform melted mixture at 110°C. This melted mixture was sprayed under pressure into a rotary cylindrical granulating apparatus At the same time as the spraying, 2000 parts of a recycled material having the same composition as the melt was also fed to the granulation apparatus and the whole mixture was granulated whilst being tumbled. The temperature of the produce withdrawn from the granulating apparatus was 75°C. and the water content of the product was 1.6%. The granulated product was then introduced into a rotary cooler, was cooled with air maintained at room temperature and was then sieved to obtain 1000 parts of a granular product which passed a 5 to 12 mesh screen. The surface of the granules were smooth and spherical and the granules had the following composition:

	H_2O	TN (total N)	UN (urea N)	AN (ammonia N)	K_2O
%	1.3	23.2	23.1	0.1	18.5

When the degree of caking of this product was compared with that of commercial NK fertilizer having the composition 1.2% H_2O, 14.3% AN, 1.3% NN and 15.6% K_2O), it was found that the degree of caking for the commercial fertilizer was 2.6 kg., whereas that of the product of this Example was 0.8 kg.

EXAMPLE 2

850 Parts of urea (46.0% UN), 50 parts of potassium chloride (61% K_2O) and 100 parts of gypsum ($CaSO_4 . 2H_2O$) were mixed and heated at 110°C. to produce a fluid uniform melted mixture at 110°C. This melted mixture was sprayed under pressure into a rotary cylindrical granulating apparatus, to which there was added at the same time 2000 parts of a recycled material having the same composition as the melted mixture and the whole mixture was granulated whilst being tumbled. The temperature at the outlet of the granulating apparatus was 76°C. and the water content of with withdrawn product was 1.4%. The granulated product was then introduced into a rotary cooler, was then cooled with air maintained at room temperature and then sieved to obtain 980 parts of granular product which passed a 5 to 12 mesh screen. The surface of the product was smooth and spherical and the composition of the product was as follows:

	H_2O	TN	UN	AN	K_2O
%	1.2	38.4	38.3	0.1	3.1

EXAMPLE 3

250 Parts of urea (46.0% UN), 440 parts of potassium chloride (61.0% of K_2O) and 390 parts of gypsum ($CaSO_4 . 2H_2O$) were mixed and heated at 115°C. to produce a fluid uniform melted mixture. This melted mixture was sprayed under pressure into a rotary cylindrical granulating apparatus to which there had been added, at the same time, 2000 parts of a recycled material having the same composition as the melted mixture and the whole mixture was granulated whilst being tumbled. The temperature at the outlet of the granulating apparatus was 75°C. and the water content of the withdrawn product was 1.4%. The granulated product was then introduced into a rotary cooler, was cooled with air maintained at room temperature and was then sieved to obtain 920 parts of a granular product which passed a 5 to 12 mesh screen. The surface of the product was smooth and spherical and the composition of the product was as follows:

	H_2O	TN	UN	AN	K_2O
%	1.2	11.5	11.4	0.1	26.6

The degree of caking of this product was compared with that of the commercial fertilizer described in Example 1 and it was found that whereas the former was 0.7 kg., the latter was 2.6 kg.

EXAMPLE 4

450 Parts of urea (46.0% UN), 40 parts of potassium chloride (61.0% K_2O) and 10 parts of water were mixed and heated to obtain a fluid uniform melted mixture. This melted mixture was sprayed under pressure into a rotary cylindrical granulating apparatus to which there was added at the same time 300 parts of potassium chloride 61.0% of K_2O), 250 parts of gypsum ($CaSO_4 . 2H_2O$) and 2300 parts of a recycled material having the same composition as the melted mixture and the whole mixture was granulated whilst being tumbled. The temperature of the product withdrawn from the granulating apparatus was 70°C. and the product had a water content of 1.8%. The granulated product was then introduced into a rotary cooler, cooled with air maintained at room temperature and then sieved to obtain 1000 parts of a granular product which passed a 5 to 12 mesh screen. The surface of the product was smooth and spherical and the composition of the produce was as follows:

	H_2O	TN	UN	AN	K_2O
%	1.4	20.6	20.5	0.1	20.7

EXAMPLE 5

1050 Parts of a melted mixture having the same composition as that employed in Example 1 were sprayed into a rotary cylindrical granulating apparatus, to which there was added at the same time, 2000 parts of a recycled material having the same composition as the melted mixture and were granulated while being tumbled to obtain 3000 parts of a granulated product. The temperature of the product withdrawn from the granulating apparatus was 75°C. and the product had a water content of 1.6%. The particle sizes of the product were as follows:

	+5 mesh	5 to 12 mesh	−12 mesh
%	5.8	45.6	48.6

Then this product was admixed with 400 parts of recycled material and then introduced into a rotary cooler and cooled with air maintained at room temperature. The granules produced had the following particle size distribution:

	+5 mesh	5 to 12 mesh	−12 mesh
%	4.0	36.5	59.5

The granules were then sieved with two sieves of 5 and 12 meshes respectively to obtain 1230 parts of a granular product having an intermediate granule diameter. The surface of the product was smooth and spherical and the composition of the product was as follows:

	H_2O	TN	UN	AN	K_2O
%	1.1	23.5	23.4	0.1	18.4

The degree of caking of this product was 0.7 kg. When the caking degree of Kumiai No. 5 NK fertilizer (of 1.2% H_2O, 14.3% AN, 1.3% NN and 15.6% of K_2O) pro-

duced by Sumitomo Chemical Co. Ltd., was measured for comparison, it was 2.6 kg.

EXAMPLE 6

980 Parts of a melted mixture having the same composition as that employed in Example 2 were spaced under pressure into a rotary cylindrical granulating apparatus, to which there was added at the same time, 2000 parts of a recycled material having the same composition as the melted mixture and were granulated whilst being tumbled to obtain 2960 parts of a granulated product. The temperature of the product withdrawn from the granulating apparatus was 76°C. and the water content of the product was 1.4%. The particle size distribution of the product was as follows:

	+5 mesh	5 to 12 mesh	−12 mesh
%	6.8	44.7	48.5

The product was admixed with 500 parts of a recycled material obtained after the product granules had been separated, introduced into a rotary cooler and cooled with air maintained at room temperature too produce powder-coated granules having the following particle size distribution:

	+5 mesh	5 to 12 mesh	−12 mesh
%	3.7	46.7	59.6

The granules were then sieved with two sieves of 5 to 12 meshes to obtain 1260 parts of a granular product having an intermediate granule diameter. The surface of the product was smooth and spherical and the composition of the product was as follows:

	H_2O	TN	UN	AN	K_2O
%	1.0	38.1	38.0	0.1	3.3

When the degree of caking of this product was measured as compared with that of the commercial fertilizer described in Example 1 it was found that the former was 1.0 kg. and the latter was 2.6 kg.

WHAT WE CLAIM IS:—

1. A process for the preparation of a granular NK fertilizer which process comprises spraying a liquid mixture of 20—90% by weight of urea, 2—50% by weight of potassium chloride, 0—40% by weight of gysum (calculated as the anhydrous salt), and 1—10% by weight of water onto solid material in a rotary granulating cylinder, the solid material being (a) a recycled material, obtained from a previous preparation of such granular material after granules of desired size have been separated therefrom or (b) a mixture of said recycled material together with one or more of potassium chloride, gypsum and urea, the nature and proportions of all the components being such as to produce a product containing 20—90% by weight of urea, 2—50% by weight of potassium chloride and 5—40% by weight of gypsum (calculated as the anhydrous salts).

2. A process as claimed in Claim 1 in which the liquid mixture is sprayed at 90° to 130°C.

3. A process as claimed in Claim 1 or Claim 2 in which the temperature of granulation is 50°—100°C.

4. A process as claimed in any of the preceding claims in which the water content of the material being granulated 1—2% by weight.

5. A process as claimed in any of the preceding claims in which the recycled material constitutes 50—90% by weight of the material being granulated.

6. A process as claimed in any of the preceding claims in which the mole ratio of urea to gypsum in the product is 4—7:1.

7. A modification of the process as claimed in any of the preceding claims in which the recycled material is divided into two parts, the first part is mixed with the sprayed mixture and the resulting admixture granulated, the second part is then admixed with the granulated product thus obtained and the resulting admixture cooled whilst being tumbled in a rotary cylinder.

8. A process as claimed in any of the preceding claims in which the liquid mixture is sprayed under a pressure of 0.1—5.0 kg/cm^2 gauge.

9. A process for the production of a fertilizer according to claims 1 and 7 and substantially as herein before described with reference to the Examples.

10. A granular fertilizer produced by the process as claimed in any of the preceding claims.

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